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(54) Method of fractional attenuation of electromagnetic radiation.

(57) A method for the protection of matter, including humans, by attenuation of electromagnetic radiation is disclosed. The method comprises providing the matter with a protective layer formed from at least two elements, or compounds thereof, selected from different specified groups. The elements provide complementary attenuation of the radiation, and may be selected to optimize protection against specific energy spectra. The elements or compounds may be in a carrier e.g. a polymer. The method may be used in a variety of ways e.g. in protection of humans from x-rays, gamma rays or other radiation, or in packaging applications, protection of equipment sensitive to radiation or the like.

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METHOD OF FRACTIONAL ATTENUATION OF ELECTROMAGNETIC RADIATION

The present invention relates to a method of shielding or protection against electromagnetic radiation, including x-rays and gamma radiation, and to compositions for protection against electromagnetic radiation that are mixtures of two or more radiation-absorbing elements, or compounds thereof, that complement each other over a range of energies.

Exposure of matter, including humans, to electromagnetic radiation, especially x-rays or alpha, beta or gamma radiation, from a wide variety of sources is increasing. Such exposure may be deliberate, for example, in the x-raying of a patient or an object, or treatment of a patient with radiotherapy or other radiation emitting devices, but the exposure to radiation may also be an occupational hazard e.g. to the operators of v-ray or other radiation emitting materials or equipment. Many steps are taken to protect workers from exposure to radiation, including the extreme step of completely separating the operator from the radiation source. However, on many occasions such separation is impractical or even impossible. For instance, it may be beneficial to have an operator in the vicinity of equipment that emits radiation, especially during treatment or diagnosis of a patient using radiation, in order to facilitate operation of the equipment and/or it may be desirable to shield a patient from radiation except in those areas where the radiation is desired.

Individual energy absorbing elements have been proposed for use as protection against or attenuation of electromagnetic radiation. The element is normally selected to reduce or prevent penetration by the highest quantum level of energy in the spectrum, usually the shortest wavelength or highest keV band. Typical methods involve the use of sheet metal, especially metallic lead or lead compounds; lead and its compounds are frequently used for protection against x-rays and beta and gamma radiation. Lead has the advantages of being readily available at low cost and it has a high density and a high atomic number, and is thus a compact absorber of medium to high energy radiation.

In embodiments, lead or compounds of lead are finely dispersed in a matrix e.g. an inert, rigid or flexible, polymeric or elastomeric material, or laminated to flexible or reinforced plastics or rubbers, or sintered into refractory lead bricks. One example of such use is disclosed in Japanese patent application No. 58-053928 of K. Yamamoto, published 1983 March 30, which discloses an elastic (rubber) foam material containing large quantities of metal constituents e.g. lead oxide; use of barium ferrite/nickel ferrite and barium ferrite/magnesium ferrite in such material for protection against magnetic effects is also disclosed. Similarly, Japanese patent application No. 57-141430 of K. Yamamoto, published 1982 September 01, discloses a leaded foam material comprising a foamed material having as its base a natural or synthetic rubber. Canadian Patent 815 609 of J. D. McCluer et al, issued 1969 June 17, discloses a flexible material comprising a fabric base and a lead-loaded elastomeric layer adhering to at least one surface of the fabric base.

Japanese patent application 61 228 051 of Dainichi Nippon Cables, published 1986 October 11, discloses compositions of ethylene copolymers that contain 5-50 parts of antimony oxide and 5-100 parts of barium sulphate, per 100 parts of polymer, as a wire coating composition that may be cross linked with electrons. U.S. Patent 4 563 494 discloses a polymer composition formed from at least one lanthanide oxide or hydroxide for use as a shield against neutron radiation. U.K Patents 1 603 654 and 1 603 655, granted 1981 November 25, disclose use of compositions of metallic lead in polyvinyl chloride as an x-ray absorption material.

In some instances, additional elements, or, compounds thereof, are added in small quantities of from about 5 ppm to less than 5%, as processing aids or as modifiers of the product obtained or to improve the metallurgical properties of lead. Such compounds are known in their respective arts as refractory aids, polymer/rubber stabilizers, alloying elements and the like, with the selection of those compounds not being related to any energy absorption properties that the elements may exhibit.

As an example, UK 2 117 964A of Amersham International, published 1983 October 19, discloses a radiation shielding brick formed from a layer of e.g. an alloy of lead that contains 4% of antimony, and a layer of a plastic material. UK 1 137 554 of A. Donath et al (Glasswell Projects), published 1968 December 27, relates to building products formed from a paste or powder of compounds containing lead mixed with an oil or epoxy resin; the lead compound may be a lead oxide or tungstate. UK 984 213 of Egon Rauschert et al, published 1965 February 24, relates to a refractory radiation protection material comprising at least 50% by weight of an inorganic lead compound and at least one inorganic compound of a rare earth metal e.g. a phosphate of cerium or monazite sand; the material is stated to have a higher temperature resistance than lead but only about half the absorption value of lead with respect to hard gamma rays.

Japanese Kokai 59 126 296 of S. Madao et al, published 1984 July 20, relates to a laminated

composition for shielding against radiation, formed from lead or lead compound in a copolymer resin laminated to plasticized polyvinyl chloride. The copolymer may contain roll releasing agents, blocking inhibiting agents and the like, while the polyvinyl chloride is exemplified as containing tin maleate and magnesium oxide.

UK 1 122 766 of S. Sedlak, published 1968 August 07, discloses a flexible radiation shielding material comprising an elastomeric matrix having filler particles distributed throughout the matrix. The filler is formed from an alloy of an ionization absorbing metal and at least one other metal. The latter is intended to overcome effects of lead compounds e.g. oxides and carbonates, that tend to be naturally present in small amounts in or on metallic lead, for instance as a result of atmospheric pollution, and which act as accelerators for various types of rubber latices; in some instances the same or related compounds are added to rubber latices to promote, catalyse or stabilize reactions e.g. cross-linking or vulcanizing of the rubber. Lead/tin and lead/antimony alloys are disclosed as overcoming such effects.

UK 954 593 of Gentex Corporation, published 1964 April 08, discloses shielding against ionizing radiation that is in the form of lead coated fabrics that have been dipped into mercury, thereby forming a lead amalgam, to impart flexibility to the coated fabric. UK 903 488 of R.F. Fraser-Smith, published 1962 August 15, discloses containers formed from tungsten metal in which particles of the tungsten metal are mechanically held together by a matrix of lead; the containers may be used for substances emitting harmful radiation e.g. radio-active isotopes.

UK 1 110 181 of F. Marxen et al, published 968 April 18, discloses a material that is effective as shielding against radioactive rays. The material is in the form of a body of cement or concrete having a 2.5-35% content of one or more lead, bismuth, tungsten, zirconium, iron, tin, cadmium, lithium or barium compounds of stearic acid and/or a fatty acid, and may be used as shielding against alpha, beta and gamma rays and neutron radiation.

Heavy, thick sound insulation using specific low cost barium salts to replace lead compounds is disclosed in Chinese patent application 8600457 of Liu et al. The addition of 100-3000 parts by weight of a metal, metal oxide, metal salts or fillers e.g. iron oxide, ferrite, lead oxide, tin oxide, barium or lead sulphate, barium or lead carbonate, to bituminous or bituminous/rubber compositions is disclosed in Japanese patent application 60 079 065 of Ube Industries, published 1985 May 04. Sound insulating sheet may be obtained by the coating iron foil with tin/lead, as is disclosed in Japanese patent application 60 026 651 of Riken KK, published 1985 February 09.

Radiation protection materials, especially in the form of apparel, are disclosed in the patent application of M.J. Lilley, J.M. MacLeod, G.E. Mawdsley, G.P. Reh and M. J. Yaffe filed concurrently herewith. Highly filled compositions of metal compounds in polymers for use in attenuation of energy are disclosed in the patent application of M.J. Lilley, J.M. macLeod and R.H. Servant also filed concurrently herewith.

Unless specified to the contrary, all amounts of components of compositions or protective layers specified herein are on a weight basis, calculated on the amount of primary element e.g. if the compound was barium oxide, then the amount of component would be calculated on the basis of the amount of barium.

A method for the protection of matter by attenuation of electromagnetic radiation, using compositions or protective layers formed from two or more elements having different and complementary radiation absorption characteristics, has now been found.

Accordingly, the present invention provides a method for the protection of matter by fractional attenuation of an electromagnetic radiation spectrum having energies in the range of 10-200 keV, said method comprising providing the matter with a protective layer formed from at least two elements, or compounds thereof, selected from the group consisting of actinium, antimony, barium, bismuth, bromine, cadmium, cerium, cesium, gold, iodine, indium, iridium, lanthanum, lead, mercury, molybdenum, osmium, platinum, pollonium, rhenium, rhodium, silver, strontium, tantalum, tellurium, thallium, thorium, tin, tungsten, uranium and zirconium,
each element being in an amount of at least 5% by weight of the layer, said layer consisting of at least 40% by weight of said elements, said elements being selected to have complementary absorption characteristics in at least a selected portion of said spectrum.

The present invention further provides a material for the protection of matter by fractional attenuation of an electromagnetic radiation spectrum having energies in the range of 10-200 keV, said material comprising a protective layer formed from at least two elements, or compounds thereof, selected from the group consisting of actinium, antimony, barium, bismuth, bromine, cadmium, cerium, cesium, gold, iodine, indium, iridium, lanthanum, lead, mercury, molybdenum, osmium, platinum, pollonium, rhenium, rhodium, silver, strontium, tantalum, tellurium, thallium, thorium, tin, tungsten, uranium and zirconium,
each element being in an amount of at least 5% by weight of the layer, said layer consisting of at least 40%

by weight of said elements, said elements being selected to have complementary absorption characteristics in at least a selected portion of said spectrum.

In a preferred embodiment of the method or material of the present invention, the protective layer attenuates electromagnetic radiation having energies of greater than 1 keV to an extent that is equivalent to a layer of metallic lead having a thickness of at least 0.10 mm.

In a preferred embodiment of the invention, the protective layer has at least two different elements selected such that at least one element is selected from the group consisting of:

(A) actinium, bismuth, gold, lead, mercury, pollonium, thallium, thorium and uranium;

(B) bismuth, gold, lead, mercury and thallium;

(C) iridium, osmium, platinum, rhenium, tantalum and tungsten; and

(D) bromine, molybdenum, rhodium, strontium and zirconium; and at least one element is selected from the group consisting of:

(E) barium, cerium, cesium, iodine and lanthanum; and

(F) antimony, cadmium, indium, silver, tellurium and tin, and in another preferred embodiment the protective layer has at least two different elements selected such that at least one element is selected from group (A) above and at least one element is selected from the group consisting of (B), (C), (E) and (F) above.

The invention is illustrated in the drawing (Figure 1) in which energy fluence spectra are shown for an unattenuated spectrum, for lead and for a composition of the invention.

The present invention relates to a method of protecting matter against the effects of electromagnetic radiation by fractional attenuation of the radiation using a layer of radiation protection material. In particular, the invention relates to protection against radiation of at least two different wavelengths, especially in the form of a spectrum of radiation. The combination of elements, or compounds thereof, forming the protective layer will especially depend on the particular spectrum against which protection is required, and particularly the distribution of wavelengths in that spectrum.

As an illustration, if the spectrum is a typical spectrum in the range of 10-60 keV, a preferred protective layer comprises at least one element or compound thereof selected from groups (A), (C) and (D) above with the remainder being at least one element or compound thereof selected from groups (E) or (F), especially 20-70 parts and in particular 30-50 parts from groups (A), (C) and (D), per 100 parts of the protective layer, on an element basis. Alternatively, if the spectrum is a typical spectrum in the range of 20-150 keV, a preferred protective layer comprises at least one element or compound thereof selected from group (A) above with the remainder being at least one different element or compound thereof selected from groups (B), (C), (E) or (F), especially 50-85 parts and in particular 60-80 parts from group (A), per 100 parts of the protective layer, on an element basis. For spectra containing radiation above 150 keV, pollonium, actinium, thorium or uranium may be combined with another different element from groups (A), (B) or (C). Similarly, for radiation having energies below 40 keV, an element from group (F) may be combined with an element from groups (A), (C) and (D).

In preferred embodiments of the invention, the protective layer is formed from at least three elements, or compounds thereof. For example, for a spectrum having radiation predominantly in the range of 10-60keV, at least one element may be selected from groups (A), (C) and (D), one element from group (E) with the remainder being selected from group(F); preferred amounts of the elements are 20-50 parts per 100 parts of the protective layer, on an element basis. Similarly, for radiation predominantly in the range of 20-150 keV, at least one element may be selected from group (A), at least one different element from groups (B) and (C), with the remainder selected from groups (E) and (F); preferred amounts are 20-50 parts per 100 parts of the protective layer, on an element basis.

By suitable selection of the combinations of the elements or compounds, including selection of the proportions of the elements, it is possible to control not only the amount of radiation that is attenuated but also the shape of the spectrum of the radiation that is transmitted through the protective layer i.e. the shape of the radiation spectrum remaining after fractional attenuation and which passes through the protective layer. Both the shape of the photon spectrum and the so-called fluence spectrum i.e. the spectrum formed by taking into account the relative energies of the transmitted radiation, are important. An illustration of a comparison of the attenuation achieved by lead and by a lead/barium tungstate (1:2 on a weight basis) composition is shown in Figure 1, which is a computer generated plot of an energy fluence spectra. Figure 1 shows the spectral curve for the unattenuated or source radiation (Curve 1) as well as the spectral curve as attenuated by a layer of lead (Curve 2) and by a layer of the lead/barium tungstate composition (Curve 3); Curves 2 and 3 represent 3.2 % transmission of energy. It will be noted that although both the lead and lead/barium tungstate composition result in a substantial amount of attenuation of the radiation, the lead/barium tungstate composition exhibits substantially higher attenuation of radiation in the 70-90 keV

range; that range is most often encountered with respect to protection of operators of x-ray equipment.

It has been found that elements may be combined in both type and proportions such that (a) the mass of elements or compounds required to absorb a predetermined fraction of the radiation from a given source may be reduced by up to about 40% by weight compared to a single element e.g. lead, or (b) for the same mass of elements, or compounds thereof, the amount of radiation absorbed is substantially higher than for a single element e.g. by up to 150% of the so-called "lead equivalency". Such properties are particularly important in the field of radiation shielding and protective apparel where better protection or the same protection at less weight of the apparel offers important benefits to the user in terms of protection and/or comfort.

In preferred embodiments of the invention, the elements are antimony, barium, bismuth, bromine, cadmium, gold, iodine, lanthanum, lead, mercury, molybdenum, rhenium, silver, strontium, tantalum, tellurium, tin, tungsten, uranium and zirconium.

The elements may be in the form of elements per se or alloys, amalgams or compounds of such elements. For example, the compounds may in the form of oxides, carbonates, sulphates, halides (especially. bromides, fluorides and iodides), hydroxides, tungstates, carbides, sulphides, uranates and tellurides, or metallic salts of organic acids e.g. acetates, stearates, naphthenates, benzoates, formates, propionates, and other organotin and organolead compounds. In the event that a compound is used to form the protective layer, and particularly where efficient radiation protection per unit mass of absorbents is required, the amount of element in the compound should be at least 70% by weight of the compound. The compounds should be compatible with any copolymer, adhesive, carrier or other supporting matrix component of the protective layer in which it is used, although there may be interactions between the components that enhance the properties of the resultant material.

Compounds or salts comprising the two, or more, required radiation absorbing elements chemically bonded together are particularly efficient radiation absorbers, per unit mass of the protective layer, since the diluent effect of non-radiation absorbing elements e.g. oxygen, sulphur etc. is avoided. Examples include antimony tritelluride, bismuth iodide, mercuric bromide and lead tungstate. For the same reason, metallic alloys or amalgams are also useful, particularly where the element has unwanted impurities, is too reactive or too costly to use in a pure form.

The protective layer may be formed in a wide variety of ways e.g. by laminating, adhering or otherwise bonding together layers, including films and foils, formed from each of the components. Alternatively, the components may be admixed and a layer formed from the admixture, especially an admixture that has been melted so that a uniform protective layer has been obtained. Layers may also be obtained by sintering, cladding or depositing e.g. by means of electrodeposition or sublimation techniques, one or more elements onto a substrate or another element. However, in many instances, the protective layer will be formed of one or more compounds of the elements, and at least one of the compounds may not be capable of being meltedor fused. In such embodiments, or for other reasons, the compounds may be admixed with a carrier e.g. a polymer, resin, elastomer or other solid material that is capable of being formed into the protective layer e.g. into films, foils or coatings. Such carriers may be thermosetting polymers or thermoplastic polymers, both of which are known in the art, or elastomers, rubbers, waxes, organic adhesives or other binders.

In embodiments in which the protective layer is produced by sintering or other use of metal powders or admixed with a carrier e.g. a polymer, the elements or compounds thereof are used in a finely divided form and are uniformly dispersed throughout the protective layer. For instance, the particle size should be less than 100 mesh (screened to an average of less than 150 microns particle size) and in particular have an average of about 200 mesh (screened to greater than 60 microns).

In embodiments in which the radiation absorbing protective layer of two or more elements is admixed, dispersed, laminated or otherwise mechanically supported by, or with, the use of non-radiation absorbing matter, the radiation absorbing component should be at least 50% and preferably at least 65% of the total weight of the protective layer. In preferred embodiments, the radiation absorbing component is at least 80% of the total weight of the protective layer.

The protective layer is used in a thickness that attenuates radiation having energies of greater than 10 keV, and is preferably the equivalent of a layer of metallic lead having a thickness of at least 0.10 mm, especially at least 0.25 mm and in particular at least 0.5 mm. Such equivalency is measured in the manner for determination of lead equivalency known in the art, using for example x-rays having a spectrum energy of, typically, a maximum of 100 kV, as described in Example I. In more general terms, equivalence is determined by measuring the broad area transmission of radiation of a sample of a protective layer for a radiation beam of known energy. The transmission is then measured in the same manner for a set of samples of commercially-pure lead of different known thicknesses, and the equivalence for the test sample

is obtained by interpolation. Such equivalence only applies to the energy spectrum used in the test measurements. For diagnostic x-ray protection, a typical energy spectrum is obtained when a potential of 100kVp (KiloVolts Peak) is applied to an x-ray tube. Transmission is defined as the ratio of the exposure (coulombs/kg-air) measured in an ionization chamber with material in the beam to the corresponding exposure obtained without material in the beam.

The nature of the protective layer is such that the layers will provide superior attenuation and hence greater protection than lead, or any other single element absorber, per unit mass of element, against radiation having energies of greater than 10 keV, preferably providing protection equivalent to 0.5 mm of lead with less mass of element or better protection at the same mass of element. The improved attenuation applies to a specific energy (wavelength) spectrum, and may be optimized, based on better protection, lower mass and/or lower cost, for each individual energy spectrum or range of spectra. The protective layers of the invention attenuate radiation and provide protection over a broader range of energies of electromagnetic radiation than does metallic lead or lead compounds, or other protective layers based on a single element.

The present invention may be used in a variety of manners. For instance, the method may be used to protect humans against the effects of x-rays or other radiation e.g. to protect operators of x-ray equipment during treatment of patients or operation of other equipment that emits radiation that is potentially harmful to a human. Furthermore, the method of the present invention may be used to protect other matter e.g. physical objects, against effects of radiation. For instance, the method may be used to provide coatings or layers of wrapping material for protection of articles during shipping or use.

The present invention is illustrated by the following examples:

Example I

Compositions of metals were prepared and tested for absorption of x-rays. Absorbence to x-rays was measured by the following procedure: Exposure rate was measured using a calibrated ionization chamber at a position 100 cm from a tungsten target x-ray tube collimated to provide a beam measuring 8 cm x 8 cm. The tube was powered by a constant-potential x-ray generator providing 100 kV at 10 mA with a resultant half-value layer (HVL) of 5.0 mm aluminum. Variation in output was less than 0.5%/hour. Samples of the compositions and of lead of known thickness were placed in the beam, 15 cm above the ionization chamber to determine the relative transmissions, and the lead equivalence for the composition was obtained by interpolation.

The compositions prepared and the results obtained were as follows:

Run No.	1	2	3
PbO (wt.%)	27	40	48
SnO (wt.%)	26.5	20	16
$BaSO_4$ (wt.%)	26.5	20	16
Carrier*(wt.%)	20	20	20
Elements in Inorganic Component (wt.%)	80	83	85
Composition Density	3.0	3.1	3.2
Lead Equivalence (mm)	0.38	0.40	0.41
Weight Saving**	22	17	14

* ethylene/vinyl acetate copolymer, unplasticized

** reduction in weight of sample, elemental basis, compared to lead to give same absorption as 0.5 mm of lead at 100 kVp.

Example II

A composition of PbO (29.75% by weight) and barium oxide (55.25% by weight) in an ethylene/vinyl

acetate copolymer (15% by weight) was prepared. X-ray absorption was measured, for 100 kVp, using the procedure of Example I.

It was found that for absorption equivalent to 0.5 mm of lead, the composition weighed 5.9 kg/m^2, or 4.54 kg/m^2 based on the amount of absorbing elements only.

Example III

A composition of PbO (22% by weight), tungsten trioxide powder (20% by weight) and barium fluoride (38% by weight) in an ethylene/vinyl acetate copolymer (17% by weight) containing 3% by weight of dioctyl phthalate was prepared. The composition had a density of 3.36 g/cm^3. The composition contained 80% by weight of filler and had a flexural modulus of 27.6 MPa.

It was found that for absorption equivalent to 0.5 mm of lead, the composition weighed 5.83 kg/m^2, or 3.85 kg/m^2 based on the amount of absorbing elements only. The elemental weight saving compared to 0.5 mm of lead was 32% and a sample weight saving compared to so-called "lead/vinyl", which has 80% lead in 20% polyvinyl chloride (w/w) and weighs 7.3 kg/m^2, of 20%.

Example IV

A composition of lead tungstate (46.75% by weight) and barium fluoride (38.25% by weight) in an unplasticized ethylene/vinyl acetate copolymer (15% by weight) was prepared. The x-ray absorption was measured using the procedure of Example I.

It was found that for absorption equivalent to 0.5 mm of lead, the composition weighed 5.9 kg/m^2, or 4.31 kg/m^2 based on the amount of absorbing elements only. The elemental weight saving compared to 0.5 mm of lead was 24% and the sample weight saving compared to lead/vinyl was 19%.

This Example illustrates a composition that does not contain a plasticizer.

Example V

A composition of metallic lead (21.675% by weight), tungsten trioxide (22.95% by weight) and barium fluoride (40.375% by weight) was prepared in Polymer I (7.50% by weight) and Polymer II (3.75% by weight) was prepared. Polymer I was a blend of stabilized polyvinyl chloride and an ethylene/butyl acrylate/carbon monoxidecopolymer, and Polymer II was an ethylene/vinyl acetate/carbon monoxide copolymer having a melt index of about 35 dg/min. The composition also contained 3.75% by weight of trioctyl trimellitate. X-ray absorption was measured using the procedure of Example I.

It was found that for absorption equivalent to 0.5 mm of lead, the composition weighed 5.48 kg/m^2. The elemental weight saving compared to 0.5 mm of lead was 31% and the sample weight saving compared to lead/vinyl was 26%.

Example VI

A composition of barium tungstate (84% by weight) was prepared in a blend of ethylene/vinyl acetate copolymers (9.5% by weight) and Sunthene 4240 processing oil as plasticizer (6.5% by weight). The polymer composition obtained had a density of 3.0 g/cm^3. X-ray absorption was measured using the procedure of Example I.

It was found that for absorption equivalent to 0.5 mm of lead, the sample weighed 5.51 kg/m^2. The elemental weight saving compared to 0.5 mm of lead was 29% and the sample weight saving Compared to lead/vinyl was 24%.

The sample of the polymer composition was in the form of sheet having a weight of 4.47 kg/m^2. X-ray absorption was measured using the procedure of Example I but at 60 kVp, 80kVp, 100 kVp and 120 kVp. At 100 kVp, the sheet was equivalent to 0.39 mm of lead; the corresponding results at 6okVp, 80 kVp and 120

kVp were 0.27 mm, 0.31 mm and 0.35 mm.

Example VII

A two-layer structure was prepared as follows: one layer was formed from powdered metallic lead in a composition of ethylene/vinyl acetate copolymer containing a plasticizer and a second layer was formed from barium tungstate in the same copolymer and plasticizer. The ratio of lead to barium tungstate in the two layers was 0.70:1 on a weight basis. The layers were placed together, and tested in the manner described herein for the testing of polymer compositions.

It was found that for absorption equivalent to 0.5 mm of lead, the sample weighed 5.20 kg/m^2. The elemental weight saving compared to 0.5 mm of lead was 30% and the sample weight saving compared to lead/vinyl was 29%.

The sample of the two-layer structure had a weight of 7.32 kg/m^2. The absorption of the structure was compared with lead over a range of spectra energies and the lead equivalence was determined. At 100 kVp, the sheet was equivalent to 0.72 mm of lead; the corresponding results at 60kVp, 80 kVp and 120 kVp were 0.68 mm, 0.63 mm and 0.57 mm.

Example VIII

A composition of lead powder (25.3% by weight), barium tungstate (43.1% by weight) and barium iodide (17.9% by weight) in a blend of ethylene/vinyl acetate copolymers (9.6% by weight) and Sunthene 4240 aromatic processing oil (4.1% by weight) was prepared. The polymer composition obtained had a density of 3.47 g/cm^3. X-ray absorption was measured using the procedure of Example I.

It was found that for absorption equivalent to 0.5 mm of lead, the sample weighed 5.31 kg/m^2. The elemental weight saving compared to 0.5 mm of lead was 30% by weight and the sample weight saving compared to lead/vinyl was 27% by weight.

Example IX

A composition of lead powder (9.0% by weight), a powdered lead/tin (50:50) alloy (35.8% by weight) and barium tungstate (44.6% by weight) in a blend of ethylene/vinyl acetate copolymers (6.3% by weight) and Sunthene 4240 aromatic processing oil (4.3% by weight) was prepared; thus, the composition contained 89.4% by weight of inorganic component. The polymer composition obtained had a density of 4.02 g/cm^3. X-ray absorption was measured using the procedure of Example I.

It was found that for absorption equivalent to 0.5 mm of lead, the sample weighed 4.6 kg/m^2. The elemental weight saving compared to 0.5 mm of lead was 29% by weight and the sample weight saving compared to lead/vinyl was 37% by weight.

Example X

A composition of a powdered tin/copper (97:3) alloy (13.8% by weight), a powdered lead/tin (50:50) alloy (50.3% by weight) and tungsten trioxide (25.4% by weight) in a blend of ethylene/vinyl acetate copolymers (6.0% by weight) and Sunthene 4240 aromatic processing oil (4.5% by weight) was prepared; thus, the composition contained 89.5% by weight of inorganic component. The polymer composition obtained had a density of 4.52 g/cm^3. X-ray absorption was measured using the procedure of Example I.

It was found that for absorption equivalent to 0.5 mm of lead, the sample weighed 5.28 kg/m^2.

The elemental weight saving compared to 0.5 mm of lead was 21% by weight and the sample weight saving compared to lead/vinyl was 28% by weight.

This example shows the use of two alloys in the composition.

Example XI

The following compositions were prepared:

Component	Composition*	
	A	B
Polymer**		
I	5.70	9.18
II	2.87	-
Plasticizer***	6.43	5.82
Filler		
PbO	23.38	23.38
WO_3	21.25	21.25
BaF_2	40.38	40.38
Density (g/cm^3)	3.39	3.39

* amounts are in wt. %

** Polymer I was an ethylene/vinyl acetate copolymer having a vinyl acetate content of 36% and a melt index of 0.8 dg/min. Polymer II was an ethylene/vinyl acetate copolymer having a vinyl acetate content of 33% and a melt index of 25 dg/min, that had been melt grafted with about 1.2% by weight of maleic anhydride.

*** The plasticizer was an aromatic processing oil, available as Sunthene 4240 processing oil from Sunoco Inc. of Toronto, Ontario, Canada.

Compositions A and B were formed by blending the components in a Brabender PlasticorderTM twin rotor mixer at 170° C. Sheets of the compounded composition were then formed by compression moulding, the sheets having a thickness of 1.59 mm.

Absorbence to x-rays was measured by the procedure of Example I.

The materials obtained above had an absorbence to x-rays equivalent to 0.58 mm of lead. It was found that the weight equivalent required to provide the absorption exhibited by 0.5 mm of lead was 5.35 kg/m^2 for both materials. This represents a weight saving, compared to lead, of 36% but a weight saving compared to so-called "lead-vinyl" of 27%.

Example XII

The following composition was prepared:

Component	Composition*
	C
Polymer**	
I	5.70
II	2.87
Plasticizer***	6.43
Filler	
PbO	46.75
$BaWO_4$	38.25

* amounts are in wt. %

** Polymer I was an ethylene/vinyl acetate copolymer having a vinyl acetate content of 36% and a melt index of 0.8 dg/min. Polymer II was an ethylene/vinyl acetate copolymer having a vinyl acetate content of 33% and a melt index of 25 dg/min, that had been melt grafted with about 1.2% by weight of maleic anhydride.

*** The plasticizer was an aromatic processing oil, available as Sunthene 4240 processing oil from Sunoco Inc. of Toronto, Ontario, Canada.

Composition C was formed by blending the components in a Banbury twin rotor high intensity mixer by feeding the components of the composition to the mixer. The composition obtained was formed into sheets using a calendering process at a processing temperature of about 50-55 ° C, the sheet having a thickness of 0.81 mm. The sheet was laminated to nylon fabric using the adhesive properties of the polymer mixture at elevated temperature.

Absorbence to x-rays was measured by the procedure of Example I. It was found that for absorption equivalent to 0.5 mm of lead, the composition weighed 5.73 kg/m^2. The elemental weight saving compared to 0.5 mm of lead was 21% and the sample weight saving compared to lead/vinyl was also 21%.

Additional tests were carried out using the procedure of Example I for the measurement of absorption to x-rays but at 60 kVp, 80 kVp, 100kVp and 120kVp and the lead equivalence was determined. At 100 kVp, the sheet tested was equivalent to 0.12 mm of lead; the corresponding results at 60kVp, 80 kVp and 120 kVp were 0.10 mm, 0.10 mm and 0.12 mm

Claims

1. A method for the protection of matter by fractional attenuation of an electromagnetic radiation spectrum having energies in the range of 10-200 keV, said method comprising providing the matter with a protective layer formed from at least two elements, or compounds thereof, selected from the group consisting of actinium, antimony, barium, bismuth, bromine, cadmium, cerium, cesium, gold, iodine, indium, iridium, lanthanum, lead, mercury, molybdenum, osmium, platinum, pollonium, rhenium, rhodium, silver, strontium, tantalum, tellurium, thallium, thorium, tin, tungsten, uranium and zirconium,
each element being in an amount of at least 5% by weight of the layer, said layer consisting of at least 40% by weight of said elements, said elements being selected to have complementary absorption characteristics in at least a selected portion of said spectrum.

2. The method of Claim 1 in which the protective layer attenuates electromagnetic radiation having energies of greater than 10 keV to an extent that is equivalent to a layer of metallic lead having a thickness of at least 0.10 mm.

3. The method of Claim 2 in which the protective layer has at least two different elements selected such that at least one element is selected from the group consisting of:
(A) actinium, bismuth, gold, lead, mercury, pollonium, thallium, thorium and uranium;
(B) bismuth, gold, lead, mercury and thallium;
(C) iridium, osmium, platinum, rhenium, tantalum and tungsten; and
(D) bromine, molybdenum, rhodium, strontium and zirconium;
and at least one element is selected from the group consisting of:

(E) barium, cerium, cesium, iodine and lanthanum; and
(F) antimony, cadmium, indium, silver, tellurium and tin.

4. The method of Claim 3 in which there are 20-70 parts of the element(s) from the group of (A), (B), (C) and (D), per 100 parts by weight of said at least two different elements.

5. The method of Claim 4 in which there are 30-50 parts of the element(s) from the group of (A), (B), (C) and (D).

6. The method of Claim 3 in which there are at least three elements, at least one from the group of (A), (C) and (D), at least one from group (E) and at least one from group (F).

7. The method of Claim 6 in which each element is present in 20-50 parts by weight, per 100 parts by weight of said at least three elements.

8. The method of any one of Claims 3-7 in which the radiation is in the range of 10-60 keV.

9. The method of Claim 2 in which the protective layer has at least two different elements selected such that at least one element is selected from group (A) and at least one element is selected from the group of (B), (C), (E) and (F), wherein:

group (A) is actinium, bismuth, gold, lead, mercury, pollonium, thallium, thorium and uranium;
group (B) is bismuth, gold, lead, mercury and thallium;
group (C) is iridium, osmium, platinum, rhenium, tantalum and tungsten;
group (E) is barium, cerium, cesium, iodine and lanthanum; and
group (F) is antimony, cadmium, indium, silver, tellurium and tin.

10. The method of Claim 9 in which there are 50-85 parts of the element from group (A), per 100 parts by weight of said at least two different elements.

11. The method of Claim 10 in which there are 60-80 parts of the element from group (A).

12. The method of Claim 2 in which there are at least three elements, at least one from group (A), at least one from the group of (B) and (C) and at least one from the group of (E) and (F), wherein:

group (A) is actinium, bismuth, gold, lead, mercury, pollonium, thallium, thorium and uranium;
group (B) is bismuth, gold, lead, mercury and thallium;
group (C) is iridium, osmium, platinum, rhenium, tantalum and tungsten;
group (E) is barium, cerium, cesium, iodine and lanthanum; and
group (F) is antimony, cadmium, indium, silver, tellurium and tin.

13. The method of Claim 12 in which there are 20-50 parts of each element, per 100 parts by weight of said at least three elements.

14. The method of any one of Claims 9-13 in which the radiation is in the range of 20-150 keV.

15. The method of Claim 2 in which one element is selected from the group consisting of pollonium, actinium, thorium and uranium and a different element is selected from the group of (A), (B) and (C), wherein:

group (A) is actinium, bismuth, gold, lead, mercury, pollonium, thallium, thorium and uranium;
group (B) is bismuth, gold, lead, mercury and thallium; and
group (C) is iridium, osmium, platinum, rhenium, tantalum and tungsten.

16. The method of Claim 15 in which the radiation is greater than 150 keV.

17. The method of Claim 2 in which one element is selected from group (F) and at least one element is selected from the group of (A), (C) and (D), wherein:

group (A) is actinium, bismuth, gold, lead, mercury, pollonium, thallium, thorium and uranium;
group (C) is iridium, osmium, platinum, rhenium, tantalum and tungsten;
group (D) is bromine, molybdenum, rhodium, strontium and zirconium; and
group (F) is antimony, cadmium, indium, silver, tellurium and tin.

18. The method of any one of Claims 2-17 in which the elements are selected from antimony, barium, bismuth, bromine, cadmium, gold, iodine, lanthanum, lead, mercury, molybdenum, rhenium, silver, strontium, tantalum, tellurium, tin, tungsten, uranium and zirconium.

19. A material for the protection of matter by fractional attenuation of an electromagnetic radiation spectrum having energies in the range of 10-200 keV, said material comprising a protective layer formed from at least two elements, or compounds thereof, selected from the group consisting of actinium, antimony, barium, bismuth, bromine, cadmium, cerium, cesium, gold, iodine, indium, iridium, lanthanum, lead, mercury, molybdenum, osmium, platinum, pollonium, rhenium, rhodium, silver, strontium, tantalum, tellurium, thallium, thorium, tin, tungsten, uranium and zirconium, each element being in an amount of at least 5% by weight of the layer, said layer consisting of at least 40% by weight of said elements, said elements being selected to have complementary absorption characteristics in at least a selected portion of said spectrum.

20. The material of Claim 19 in which the protective layer attenuates electromagnetic radiation having

energies of greater than 10 keV to an extent that is equivalent to a layer of metallic lead having a thickness of at least 0.10 mm.

21. The material of Claim 20 in which the protective layer has at least two different elements selected such that at least one element is selected from the group consisting of:
(A) actinium, bismuth, gold, lead, mercury, pollonium, thallium, thorium and uranium;
(B) bismuth, gold, lead, mercury and thallium; (C) iridium, osmium, platinum, rhenium, tantalum and tungsten; and
(D) bromine, molybdenum, rhodium, strontium and zirconium;
and at least one element is selected from the group consisting of:
(E) barium, cerium, cesium, iodine and lanthanum; and (F) antimony, cadmium, indium, silver, tellurium and tin.

22. The material of Claim 21 in which there are 20-70 parts of the element(s) from the group of (A), (B), (C) and (D), per 100 parts by weight of said at least two different elements.

23. The material of Claim 22 in which there are 30-50 parts of the element(s) from the group of (A), (B), (C) and (D).

24. The material of Claim 21 in which there are at least three elements, at least one from the group of (A), (C) and (D), at least one from group (E) and at least one from group (F).

25. The material of Claim 24 in which each element is present in 20-50 parts by weight, per 100 parts by weight of the total amount of all such elements.

26. The material of Claim 20 in which the protective layer has at least two different elements selected such that at least one element is selected from group (A) and at least one element is selected from the group of (B), (C), (E) and (F), wherein:
group (A) is actinium, bismuth, gold, lead, mercury, pollonium, thallium, thorium and uranium;
group (B) is bismuth, gold, lead, mercury and thallium;
group (C) is iridium, osmium, platinum, rhenium, tantalum and tungsten;
group (E) is barium, cerium, cesium, iodine and lanthanum; and
group (F) is antimony, cadmium, indium, silver, tellurium and tin.

27. The material of Claim 26 in which there are 50-85 parts of the element from group (A), per 100 parts by weight of said at least two different elements.

28. The material of Claim 27 in which there are 60-80 parts of the element from group (A).

29. The material of Claim 20 in which there are at least three elements, at least one from group (A), at least one from the group of (B) and (C) and at least one from the group of (E) and (F), wherein:
group (A) is actinium, bismuth, gold, lead, mercury, pollonium, thallium, thorium and uranium;
group (B) is bismuth, gold, lead, mercury and thallium;
group (C) is iridium, osmium, platinum, rhenium, tantalum and tungsten;
group (E) is barium, cerium, cesium, iodine and lanthanum; and
group (F) is antimony, cadmium, indium, silver, tellurium and tin.

30. The material of Claim 29 in which there are 20-50 parts of each element, per 100 parts by weight of said at least three elements.

31. The material of Claim 20 in which one element is selected from the group consisting of pollonium, actinium, thorium and uranium and a different element is selected from the group of (A), (B) and (C), wherein:
group (A) is actinium, bismuth, gold, lead, mercury, pollonium, thallium, thorium and uranium;
group (B) is bismuth, gold, lead, mercury and thallium; and
group (C) is iridium, osmium, platinum, rhenium, tantalum and tungsten.

32. The material of Claim 20 in which one element is selected from group (F) and at least one element is selected from the group of (A), (C) and (D), wherein:
group (A) is actinium, bismuth, gold, lead, mercury, pollonium, thallium, thorium and uranium;
group (C) is iridium, osmium, platinum, rhenium, tantalum and tungsten;
group (D) is bromine, molybdenum, rhodium, strontium and zirconium; and
group (F) is antimony, cadmium, indium, silver, tellurium and tin.

33. The material of any one of Claims 20-32 in which the elements are selected from antimony, barium, bismuth, bromine, cadmium, gold, iodine, lanthanum, lead, mercury, molybdenum, rhenium, silver, strontium, tantalum, tellurium, tin, tungsten, uranium and zirconium.

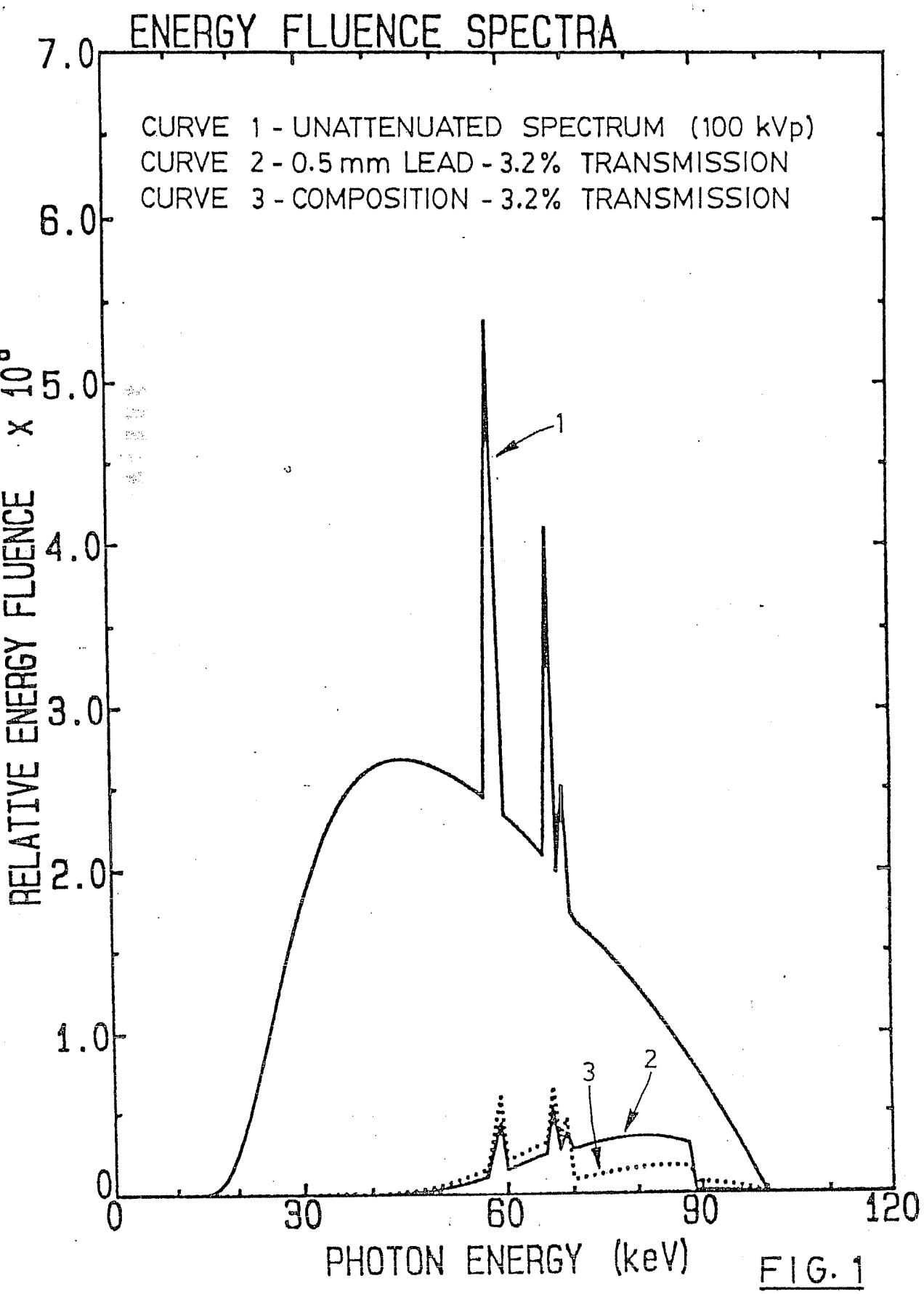
ENERGY FLUENCE SPECTRA
CURVE 1 - UNATTENUATED SPECTRUM (100 kVp)
CURVE 2 - 0.5 mm LEAD - 3.2% TRANSMISSION
CURVE 3 - COMPOSITION - 3.2% TRANSMISSION
RELATIVE ENERGY FLUENCE X 10⁸
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
0
30
60
90
120
PHOTON ENERGY (keV)
1
2
3

FIG. 1